



June 1996



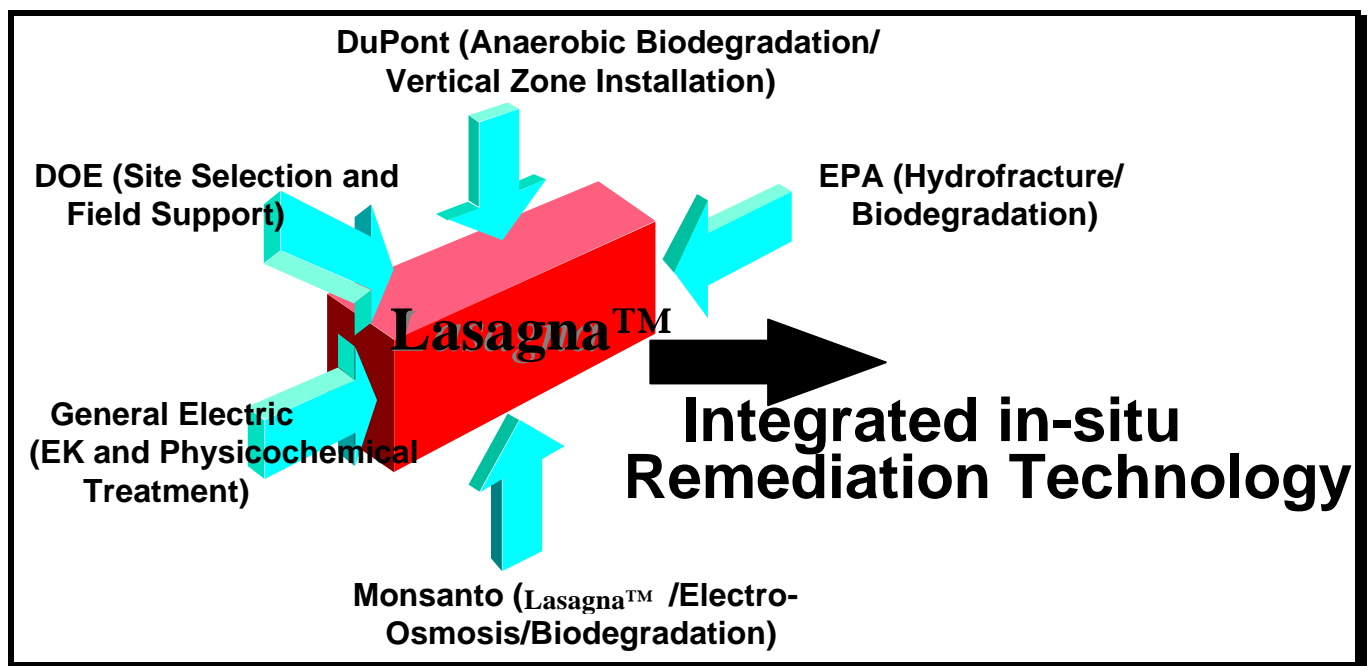
Development of an Integrated *in-situ* Remediation Technology

Topical Report for *Tasks #8 and 10* entitled “*Laboratory and Pilot Scale Experiments of the Lasagna™ Process*”
(September 26, 1994 - May 25, 1996)

Sa V. Ho, Christopher J. Athmer, and P. Wayne Sheridan (Monsanto Company)
and

Andrew P. Shapiro (General Electric Company)

DOE Contract Number: DE-AR21-94MC31185



Submitted to:

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Morgantown Energy Technology Center
Morgantown, West Virginia

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20 March, 1997

Re: Ordering Information for "*Development of an Integrated in-situ Remediation Technology*"
Topical Reports generated under DOE contract number DE-AR21-94MC31185 which was
signed September 26, 1994.

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(continued on next page)

Title	Document Number
<ul style="list-style-type: none"> • Topical Report for Task #1 entitled "Evaluation of Treatment Zone Formation Options" (September 26, 1994 - May 25, 1996) Stephen H. Shoemaker, Richard C. Landis, Ronald J. Griffith, Dale S. Schultz, and Gary E. Quinton (DuPont Company) 	DOE/METC/31185 —5436, DE97002165
<ul style="list-style-type: none"> • Topical Report for Tasks #2-4 entitled "Electrokinetic Modeling" (September 26, 1994 - May 25, 1996) Andrew P. Shapiro (General Electric Company) 	DOE/METC/31185 —5391, DE97002135
<ul style="list-style-type: none"> • Topical Report for Task #5 entitled "Cost Analysis" (September 26, 1994 - May 25, 1996) Gary Quinton, Dale Schultz, Richard Landis, Ronald Griffith, and Stephen Shoemaker (DuPont Company) 	DOE/METC/31185 —5389, DE97002134
<ul style="list-style-type: none"> • Topical Report for Task #6 entitled "Lab-Scale Development of Microbial Degradation Process" (September 26, 1994 - May 25, 1996) J. Martin Odom (DuPont Company) 	DOE/METC/31185 —5388, DE97002130
<ul style="list-style-type: none"> • Topical Report for Task #7 entitled "Development of Degradation Processes" (September 26, 1994 - May 25, 1996) M. J. Brackin, M. H. Heitkamp and S. V. Ho (Monsanto Company) 	DOE/METC/31185 —5495, DE97002165
<ul style="list-style-type: none"> • Topical Report for Tasks #8 and 10 entitled "Laboratory and Pilot Scale Experiments of the <i>Lasagna</i>TM Process" (September 26, 1994 - May 25, 1996) Sa V. Ho, Christopher J. Athmer, and P. Wayne Sheridan (Monsanto Company) and Andrew P. Shapiro (General Electric Company) 	DOE/METC/31185 —5375, DE97002150
<ul style="list-style-type: none"> • Topical Report for Task #9-Part I entitled "TCE Degradation Using Non-Biological Methods" (September 26, 1994 - May 25, 1996) Andrew P. Shapiro, Timothy M. Sivavec, and Sunita S. Baghel (General Electric Company) 	DOE/METC/31185 —5392, DE97002133
<ul style="list-style-type: none"> • Topical Report for Task #9 - Part II entitled "TCE Degradation Using Non-Biological Methods" (September 26, 1994 - May 25, 1996) Robert G. Orth and David E. McKenzie (Monsanto Company) 	DOE/METC/31185 —5393, DE97002131

(continued on next page)

<ul style="list-style-type: none">• Topical Report for Task #11 entitled "Evaluation of TCE Contamination Before and After the Field Experiment" (September 26, 1994 - May 25, 1996) B. Mason Hughes, Sa V. Ho, Christopher J. Athmer, and P. Wayne Sheridan (Monsanto Company) Stephen H. Shoemaker and John R. Larson (DuPont) Jay L. Clausen (LMES) and John L. Zutman (ORNL-Grand Junction)	DOE/METC/31185 —5496, DE97002166
<ul style="list-style-type: none">• Topical Report for Tasks #12 and 13 entitled "Large Scale Field Test of the <i>Lasagna</i>TM Process" (September 26, 1994 - May 25, 1996) Christopher J. Athmer, Sa V. Ho, B. Mason Hughes, P. Wayne Sheridan, and P. H. Brodsky (Monsanto Company) Andrew P. Shapiro, Roy F. Thornton, and Joseph J. Salvo (General Electric Company) and Dale S. Schultz, Richard C. Landis, Ron Griffith, and Stephen H. Shoemaker (DuPont)	DOE/METC/31185 —5390, DE97002156

A. Executive Summary

Development of an Integrated *in-situ* Remediation Technology

DOE Contract Number: DE-AR21-94MC31185

Topical Report for *Tasks #8 and #10* entitled: “Laboratory and Pilot Scale Experiments of LasagnaTM Process”

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Abstract: Contamination in low permeability soils poses a significant technical challenge to in-situ remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing in-situ treatments such as bioremediation, vapor extraction, pump and treat rather ineffective when applied to low permeability soils present at many contaminated sites. This technology is an integrated in-situ treatment in which established geotechnical methods are used to install degradation zones directly in the contaminated soil and electro-osmosis is utilized to move the contaminants back and forth through those zones until the treatment is completed. This topical report summarizes the results of the lab and pilot sized LasagnaTM experiments conducted at Monsanto.

A. Executive Summary (Cont'd)

Experiments were conducted with kaolinite and an actual Paducah soil in units ranging from bench-scale containing kg-quantity of soil to pilot-scale containing about half a ton of soil having various treatment zone configurations. The obtained data support the feasibility of scaling up this technology with respect to electrokinetic parameters as well as removal of organic contaminants. A mathematical model was developed that was successful in predicting the temperature rises in the soil. The information and experience gained from these experiments along with the modeling effort enabled us to successfully design and operate a larger field experiment at a DOE TCE-contaminated clay site.

B. Acronyms and Abbreviations

~	approximately
A	area (cross sectional)
ADAC	brand name of the computer input card
A/D	analog to digital computer input card
C	specific heat of the soil
C_w	specific heat of the pore water
DC, dc	direct current
DOE	Department of Energy
e-	electrons
E_o	electrochemical reduction potential
EPA	Environmental Protection Agency
ESC	Monsanto's Environmental Sciences Center
Fe	Iron
Fe^0	Iron metal
Fe^{2+}	oxidized iron (ferrous ion)
GAC	granular activated carbon
GE	General Electric
H^+	hydrogen ion
H_2O	water
HPLC	high performance liquid chromatography
I	current (amps)
ID	internal diameter
i_e	voltage gradient
k	thermal conductivity
k_e	coefficient of electroosmotic conductivity
k_h	coefficient of hydraulic conductivity
k_i	coefficient of electroosmotic efficiency
L	dimension of length
μ	viscosity of pore water
MMES	Martin Marietta Energy Systems
n	soil porosity
Na^+	sodium ion
NaOH	sodium hydroxide
O_2	oxygen
OH^-	hydroxide anion
ORNL	Oak Ridge National Laboratory
PC	personal computer
PGDP	Paducah Gaseous Diffusion Plant
pH	measure of acid content
PNP	paranitrophenol
pv	pore volumes

B. Acronyms and Abbreviations (Cont'd)

Q	volumetric flow rate
ρ	density of the soil
ρ_w	density of the pore water
ROA	Research Opportunity Announcement
σ	electrical conductivity
t	time
T	temperature
TCE	trichloroethylene
u	velocity of the pore fluid
WKWMA	Western Kentucky Wildlife Management Area
Φ	electrical potential

C. Units

amps	amperes
°C	Celsius, degrees Celsius
cm	centimeters
g, gm	grams
hr	hours
in, "	inches
kg	kilograms
kwh	kilowatt-hours
L	liters
m	meters
mA	milliamps
mg	milligrams
mho	semens or 1/ohms
ml	milliliters
μs	microsemens
μg	micrograms
N	equivalents per liter (normal or normality)
nm	nanometers
ppb	parts per billion (μg/kg)
ppm	parts per million (mg/kg)
s, sec	seconds
V	volts
wt%	percent by weight

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Statement of the Problem

Contamination in low permeability soils poses a significant technical challenge to *in-situ* remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing *in-situ* treatments such as bioremediation, vapor extraction, and pump and treat, rather ineffective when applied to low permeability soils present at many contaminated sites.

The Solution

The proposed technology combines electro-osmosis with treatment zones that are installed directly in the contaminated soils to form an integrated *in-situ* remedial process. Electro-osmosis is an old civil engineering technique and is well known for its effectiveness in moving water uniformly through low-permeability soils with very low power consumption.

Conceptually, the integrated technology could treat organic and inorganic contamination, as well as mixed wastes. Once developed, the technology will have tremendous benefits over existing ones in many aspects including environmental impacts, cost effectiveness, waste generation, treatment flexibility, and breadth of applications.

Consortium Description

A Consortium has been formed consisting of Monsanto, E. I. du Pont de Nemours & Co., Inc. (DuPont) and General Electric (GE), with participation from the Environmental Protection Agency (EPA) Office of Research and Development and the Department of Energy (DOE) Environmental Management Office of Science and Technology. The five members of this group are leaders in their represented technologies and hold significant patents and intellectual property which, in concert, may form an integrated solution for soil treatment. The Consortium's activities are being facilitated by Clean Sites, Inc., under a Cooperative Agreement with EPA's Technology Innovation Office. A schematic diagram of the government/industry consortium is shown on the front page of this topical report.

Management Plan

A Management Plan for this project was prepared by Monsanto and submitted on November 30, 1994. That plan summarized the work plan which was developed in conjunction with DuPont, GE, EPA's Risk Reduction Engineering Laboratory (RREL), Martin Marietta Energy Systems (MMES), and the Department of Energy. The DOE Gaseous Diffusion Plant in Paducah, Kentucky, was chosen as the site for the initial field tests.

CDM Federal Programs Corporation was chosen to provide the on-site support of the field tests which were installed at the DOE site in November 1994. This experiment tested the combination of electro-osmosis and *in-situ* sorption in the treatment zones. In 1994 and 1995, technology development was carried out under the present contract by Monsanto, DuPont, and GE. These studies

evaluated various degradation processes and their integration into the overall treatment scheme at bench and pilot scales.

Technical Deliverables

Tables E1 and E2 summarize the 13 technical tasks and the 8 topical reports which will be written describing the results obtained in the technical tasks. These two tables show which organization is primarily responsible for the tasks and for preparing the topical reports. The present topical report summarizes the results of tasks 8 and 10.

Table E1. List of Tasks and Responsible Company

Task	Company
Task 1 - Evaluation of Treatment Zone Formation Options	DuPont
Task 2 - Electrokinetic Model Validation and Improvement	GE
Task 3 - Design Guidance for Field Experiments	GE/DuPont
Task 4 - Analysis of Electrode Geometry and Soil Heterogeneity	GE/DuPont
Task 5 - Cost Analysis	DuPont/Monsanto
Task 6 - Lab-Scale Development of Microbial Degradation Process	DuPont
Task 7 - Lab-Scale Electrokinetic and Microbial Degradation	Monsanto
Task 8 - Lab-Scale Tests of Lasagna Process Using DOE Paducah Soil	Monsanto
Task 9 - TCE Degradation Using Non-Biological Methods	GE/Monsanto
Task 10 - Bench- and Pilot-Scale Tests	Monsanto
Task 11 - Establish Contamination Conditions Before and After Tests	Monsanto/DuPont/ MMES
Task 12 - Design and Fabrication of Large-Scale Lasagna Process	Monsanto/DuPont/ Nilex
Task 13 - Large-Scale Field Test of Lasagna Process	Monsanto/CDM

Table E2. List of Topical Reports and Responsible Company

Topical Report	Company
Task 1 - Evaluation of Treatment Zone Formation Options	DuPont
Tasks 2 - 4 Electrokinetic Modeling	GE
Task 5 - Cost Analysis	DuPont
Task 6 - Laboratory-Scale Microbial Degradation	DuPont
Tasks 7 - Lab-Scale Electrokinetic and Microbial Degradation	Monsanto
Tasks 8 and 10 - Bench and Pilot Scale Tests of Lasagna Process	Monsanto
Tasks 9 - TCE Degradation Using Non-Biological Methods	GE
Task 11 - Contamination Analysis, Before and After Treatment	Monsanto
Tasks 12 and 13 - Large-Scale Field Test of Lasagna Process	Monsanto

F. Topical Report for Tasks #8 and 10

INTRODUCTION

We have been developing a novel *in situ* technology aimed at cleaning up contamination in low-permeability soils or heterogeneous soils containing low-permeability zones. Our approach involves the synergistic coupling of electrokinetics (1-9) with in situ treatment processes. The general concept is to use electrokinetics to transport contaminants from the soil into “treatment zones” where the contaminants are removed from the pore water by sorption, immobilization or degradation. This integrated technology has been described elsewhere (10). Briefly, it consists of the following components:

- a) create permeable zones in close proximity sectioned through the contaminated soil region, and turn them into sorption/degradation zones by introducing appropriate materials (sorbents, catalytic agents, microbes, oxidants, buffers, etc.).
- b) utilize electrokinetics to transport contaminants from the soil into the treatment zones.
- c) periodic reversal of the electro-osmotic flow and recycle of the cathode effluent back to the anode side can be utilized to minimize complications associated with long-term operation of uni-directional electrokinetic processes.

Electrodes and treatment zones can be of any orientation depending upon the emplacement technology used and the site/contaminant characteristics. Schematic diagrams of two typical configurations, horizontal and vertical, are shown in Figure 1. The process has been called “LasagnaTM” (10-11) due to the layered configuration of electrodes and treatment zones.

Conceptually, the LasagnaTM technology exhibits a high degree of flexibility in the treatment process used, which can incorporate mixtures of different treatment materials in the same treatment zone or utilize functionally distinct treatment zones. The technology can thus be potentially effective for treating organic (e.g., chlorinated solvents) or inorganic (e.g., heavy metals) contamination as well as mixed wastes. With electrokinetics as the mechanism for contaminant transport, the technology is well suited for treating contaminated low permeability soils (clayey, silty soils) or heterogeneous soils (clay lens in permeable soils). Hydrofracturing (12) is a particularly attractive tool for installing horizontal electrodes and treatment zones to handle deep contamination, but does require overconsolidated soils to be effective. For shallow contamination (< 50 feet) and especially if the soil is not overconsolidated, vertical treatment approach using sheet piling or trenching may be more appropriate.

A consortium of industry and federal agencies has been formed to combine expertise and resources for accelerating the development of this technology. A field test of the process was successfully completed at a DOE site in Paducah, KY, which has clayey soil contaminated with trichloroethylene (TCE). In support of this program, we studied the movement of water and contaminants through kaolin clay and Paducah soil using the LasagnaTM process. The process was extensively studied at the bench level, then scaled up in a laboratory pilot unit. The pilot scale experiments played an important role in the

development of models and designs for the field tests. Electrokinetic characteristics, soil temperature, cathode effluent pH and conductivity, and ion electromigration were evaluated under controlled conditions. This paper focuses on the scale-up aspects of the LasagnaTM process from bench to pilot scale. Bench-scale study of various LasagnaTM configurations including heterogeneous soil matrices and coupling electrokinetics with *in-situ* biotreatment has been reported elsewhere (10).

MATERIALS AND METHODS

Bench Scale

The bench scale unit has been described in detail elsewhere (10). Briefly, the electrokinetic cell was made from clear plastic tube, 10 cm ID (81 cm² cross-sectional area). Kaolinite or Paducah soil was sandwiched between sand and/or granular activated carbon “treatment zones”. The outermost treatment zones functioned primarily as the hydraulic input and output zones. Well water or recycled cathode fluid was introduced at the anode treatment zone under constant head using a Marriotte bottle. The cathode fluid was expelled at the top of the cathode treatment zone and put into the Marriotte bottle. A plug of glass wool in the inlet/outlet fittings prevented solid material from leaving the unit. The center treatment zones contained some mixture of sand and GAC. The center “contaminated soil” section was approximately 6.5 cm long and outer soil zones were approximately 4.6 cm long. The electrodes were made of 1/4” steel plates with stainless steel rods screwed into the edge of the steel plates for connections to the power supply. The distance between the plate electrodes was 18 cm. Figure 2 shows a diagram of the bench-scale electrokinetic cell.

Pilot Scale

A pilot-scale LasagnaTM unit (Figure 3) was constructed from a Nalgene® polyethylene tub (120 cm long by 60 wide by 60 deep) to simulate the vertical LasagnaTM configuration to be used at the DOE Paducah site. Electrodes were made of 1/4 in. steel plate 59.5 cm wide by 51 cm tall. These electrodes were placed at each end of the polyethylene tub and were connected to the power leads by 12 gauge wire. Immediately in front of each electrode was a permeable zone to allow inflow and outflow of liquid to the electrode region. The permeable zones were constructed the same way as the treatment zones described below.

Treatment zones were constructed in three configurations. In the kaolinite experiments, each treatment zone consisted of 13.6 kg of medium sand and 100 grams of granular activated carbon (GAC). Sand and carbon were contained between sheets of 0.3 cm thick porous polypropylene measuring 59.5 cm wide by 51 cm tall and approximately 2.5 cm apart. There were a total of four treatment zones, two in the center of the bed and two in front of the electrodes. The distance between the two adjacent treatment zones was 35.6 cm.

Subsequent runs used treatment zones constructed by Wickdrain Inc. These treatment zones were made by gluing egg-crate polyethylene sheets to steel frames which had holes drilled to allow water

passage. The wickdrain was then wrapped with a geotextile and filled with 100% GAC. These zones were placed 35.6 cm apart and were 59.5 cm wide by 60 tall. The last Paducah soil pilot experiment used Monsanto Hydraway® construction wicking material filled with GAC and had a single treatment zone in the center in order to increase the treatment zone spacing to 53 cm.

Once the treatment zones were installed in the unit, Georgia kaolinite clay (air-dried, air-floated kaolinite obtained from Thiele Kaolinite Co., Wrens, GA) or Paducah soil was placed in the unit between the treatment zones. The first 2 pilot runs were prepared with kaolin clay packed to a depth of 43 cm. Kaolin powder was hydrated with tap water in a wheelbarrow to a water content of 37.5 wt%. All other pilot runs used Paducah soil obtained from the Western Kentucky Wildlife Management Area (WKWMA), adjacent to the DOE Paducah Plant site where the field trial was conducted. Some characteristics of kaolinite and the Paducah soil are listed in Table 1. The Paducah soil is classified as clay loam, with fairly low organic content and much higher cation exchange capacity than kaolinite.

After the soil was packed in the unit for the first pilot run, holes were drilled into the side of the tub to allow access to the treatment zones for sampling and to allow water to recycle from the cathode zone back to the anode zone. Plumbing consisted of stainless steel tubing fittings and 1/4 in. polyethylene tubing.

For studying contaminant transport, five sausage-like units of paranitrophenol (PNP) contaminated clay were placed in the center section of the pilot unit. The sausages, approximately 25 cm long and 3.8 cm in diameter, were uniformly contaminated to 370 µg PNP/g wet soil for a total of 0.94 gram PNP. Dialysis membrane was used to encase the PNP contaminated clay for convenient retrieval and analysis during and after the test. Four of the five sausages were placed horizontally in the center clay zone reaching nearly from treatment zone to treatment zone and centered in the four quadrants (looking at a cross sectional face). The fifth sausage was placed vertically in the unit, in the center of the middle clay zone.

A type "J" thermocouple was installed near the center of the unit to monitor temperature effects on the last Paducah soil test. The temperature was read using a hand held digital thermometer (Fluke Model 51) calibrated at the ice point (0 °C).

Analytical and Data System

The pilot unit was powered by a Sorenson DCR 300-9B power supply capable of 300 volts dc and 10 amp output. The voltage, current and various incremental voltages of the pilot unit were monitored and logged manually as well as with a data acquisition unit featuring a personal computer running LabTech Notebook software and a ADAC A/D voltage measurement card and line isolators.

The pore fluid from the treatment zones was analyzed periodically for specific conductance and pH. Conductance was measured using a Cole Parmer model 19101 specific conductance meter. A Corning model 140 meter and Orion model 91 series electrode were used to measure pH.

The analysis of the model organic contaminant PNP involved extracting PNP from clay samples with 0.1N NaOH solution and measuring the level of PNP in solution by spectrophotometric absorption at 400 nm or by high performance liquid chromatography (HPLC). One extraction was sufficient to remove all PNP from clay. For carbon, which binds PNP much more tightly, the extraction solution contained 0.1N NaOH and 2 wt% methylene chloride, and repeated extractions were carried out to maximize PNP recovery.

Electro-osmotic flow rate for the kaolinite experiments was measured by diverting the recycle flow into a graduated cylinder or flask. A Turbo model Magmeter MG911/F3 flow meter was installed in the recycle line for the Paducah soil runs. The meter controller unit was equipped with a 0-5 volt dc output which was connected to the data system. The meter calibration was checked in the lab at flow rates of 0, 60 and 500 ml/hr.

Electrokinetic Parameters

For each run, the electro-osmotic permeability can be calculated using the following equation:

$$Q = k_e i_e A \quad (1)$$

where;

Q : volumetric flow rate by electro-osmosis (cm³/sec)

k_e : coefficient of electro-osmotic permeability (cm²/volt-sec)

i_e : voltage gradient applied across the soil mass (volt/cm)

A : cross-sectional area perpendicular to flow (cm²)

Note that the electro-osmotic flow is proportional to the applied voltage gradient, and that the electro-osmotic permeability has the units of velocity over field strength (cm/sec over volt/cm). The coefficient of electro-osmotic transport efficiency, k_i, is by definition:

$$k_i = Q / I \quad \text{where } I : \text{current (amp)} \quad (2)$$

Combined with equation 1 and with simple rearrangement, equation 2 becomes:

$$k_i = k_e / \lambda \quad (3)$$

where λ is the conductivity of the soil column (mho/cm). The transport efficiency k_i has the units of cm³/amp-sec and reflects the efficiency of current usage for pumping water through the soil column.

RESULTS AND DISCUSSION

Scale-up experiments using the pilot unit were carried out first with kaolinite as the model soil whose electrokinetic characteristics have been well studied in our laboratory as well as by other researchers. Subsequent studies were then conducted using the actual Paducah soil.

KAOLIN CLAY

Electrokinetic Characteristics - Bench/Pilot Comparison. A large number of experiments were conducted with bench-top electro-osmosis units to provide data for designing the pilot unit. Bench-scale results for kaolinite have been reported elsewhere (10). The pilot unit was 6 times longer, 32 times larger in cross sectional area, and 197 times more volume between the two treatment zones.

The kaolinite pilot unit was operated at constant voltage for 36 days with one polarity reversal. In the first pass, liquid flow equivalent to 0.87 pore volume of the center zone was obtained in 19 days. The polarity was then reversed for 17 days passing 1.0 pore volume. The results are shown in Table 2, which also lists the corresponding data for a typical benchtop run for comparison. Average liquid flow rate for the entire pilot run was 120 ml/hr, equivalent to an average electro-osmotic permeability (k_e) of $1.7 \times 10^{-5} \text{ cm}^2/\text{V-sec}$.

The average transport efficiency (k_i) was $0.46 \text{ cm}^3/\text{amp-sec}$; and the total power consumption was 51 kwh/m^3 per pore volume (pv) of liquid. Note that the power consumption in $\text{kwh/m}^3\text{-pv}$ should be proportional to the treatment zone spacing, which explains the 5x increase in the power usage for the pilot unit vs. bench due to the corresponding 6-fold increase in the zone spacing. Table 2 shows that electro-osmosis in the LasagnaTM configuration scales up reasonably well for kaolinite clay.

PNP Removal. The effectiveness of the LasagnaTM process for removing PNP as the model organic contaminant from clay in the pilot unit was studied. Five sausage-like units of PNP contaminated clay were placed in the center section of the pilot unit, four horizontally and one vertically as described in the Experimental section.

The unit was operated for 14 days in one direction resulting in a 0.94 pore volume of water exchange in the center clay section. A single horizontal PNP contaminated sausage and some kaolinite soil surrounding the sausage were removed and analyzed for PNP. The results showed that over 98% of the PNP loaded had been removed from the sausage in this single pass. Only 15 mg/kg PNP was detected at the downstream end, with decreasing PNP concentration toward the upstream end, which contained no PNP (Figure 4).

The PNP contaminated sausage was returned to the unit. Electrical polarity was then reversed and maintained for 25 days sweeping an additional 1.6 pore volume. After that, all sausages, as well as representative samples from the center clay zone and the complete sand/carbon treatment zones were

extracted and analyzed for PNP. No detectable (<10 ppb) amount of PNP was found in any clay samples. All the PNP recovered was from the carbon in the center treatment zones. Of the PNP recovered, 91% was found in the downstream treatment zone illustrating the efficiency of the first pass.

However, only 55% of the estimated PNP loaded was recovered in the treatment zones. Although close to 100% PNP recovery was common in bench scale units, where PNP loading was typically at 100 mg PNP/g carbon, it is more difficult to extract all the adsorbed PNP when the PNP to carbon ratio is as low as it was in the pilot unit (<5 mg PNP/g carbon). Despite the low mass balance, the fact that PNP was uniformly and completely removed from the clay zones is indicative of the effectiveness of the technology for cleanup of organic contaminants like PNP. Due to the extremely low vapor pressure of PNP, it is unlikely the PNP losses were due to volatilization.

PADUCAH SOIL

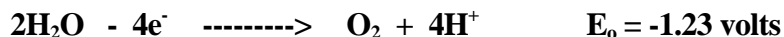
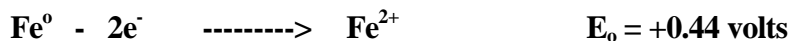
Electrokinetic Characteristics - Bench/Pilot Comparison. Paducah soil was used to study the electrokinetic characteristics of a real soil. As with kaolinite, many benchtop experiments were conducted prior to the pilot runs described here. Parameters monitored during these runs include soil temperature, pH, conductivity, and ions profiles. With two treatment zones in the center, the Paducah soil pilot unit was nearly 7 times longer, 37 times larger in cross sectional area, and 250 times more pore volume per soil zone than the bench scale unit (Table 3). Prefabricated treatment zones contained 100% granular activated carbon (GAC) instead of a mixture of sand and carbon as in the kaolinite experiments.

The Paducah soil pilot unit was operated at constant voltage for a total of 44 days with one polarity reversal. In the first pass, liquid equivalent to 0.71 pore volume of the center zone flowed in 21 days. The polarity was then reversed for 23 days passing 1.5 pore volumes. The average electro-osmotic permeability (k_e) for the first pass was $5.6 \times 10^{-6} \text{ cm}^2/\text{V-s}$, comparable to the bench-scale data, but was much higher ($10.6 \times 10^{-6} \text{ cm}^2/\text{V-s}$) for the reversed pass. The reason for this large difference is not clear. We suspected that the increased soil moisture content of this fairly dry soil (19% moisture) may have played a major role in the observed discrepancy. The average transport efficiency (k_i) was $0.22 \text{ cm}^3/\text{amp-sec}$, and the total power consumption was 200 kwh/m^3 per pore volume of liquid, about 4 times that of kaolinite. Table 3 shows that the Paducah soil appears to scale up reasonably well with respect to power consumption, which should be proportional to the treatment zone spacing.

Bipolar Effects. With the treatment zones containing 100% activated carbon, which is electrically conducting, there was the possibility of them acting as bipolar electrodes due to the applied electric field. That is, the side of the carbon zone facing the anode could behave like a cathode (which would generate OH^- and release hydrogen), and the other side of the carbon may behave like an anode (which would generate H^+ and release oxygen). Evidence for bipolar effects in terms of voltage distribution and pH are shown in Figures 5. Voltage drop typically tends to be higher near the cathode and lower near the anode (10), a pattern observed for the two treatment zones in this case. The pH's of the soil on the "anode" sides of the treatment zones were low, and those on the "cathode" sides were high, consistent with pH characteristics of the electrodes.

Larger Treatment Zone Spacing. The pilot unit was packed with fresh Paducah soil and the Monsanto Hydaway® treatment zones in a configuration that closely resembled the field design. A single treatment zone in the center of the unit and two electrode treatment zones were used. The Hydaway® zones were now spaced 53.3 cm apart. The unit was initially operated at 0.5 V/cm, which ran stable in one direction for 105 days with an average electro-osmotic permeability (k_e) of 1.1×10^{-5} cm²/volt-sec. Apparently, at this low voltage gradient the recycle of the cathode effluent back to the anode side was sufficient to stabilize the electro-osmosis process without the need for polarity reversal. Figure 6 shows the values for flowrate and current during the three months of operation.

Conductivity and pH. The pH and specific conductance of the cathode effluent and of the water in the treatment zones were monitored during the course of operation. Within a few days, the specific conductance of the fluid in the cathode zone rose sharply. Ions analysis showed that this increase in solution conductivity was due to the presence of Na⁺ (Figure 7). Sodium ion apparently moved faster than the water and accumulated in the cathode region. The advantage of the LasagnaTM process is evident here: cations transported by electromigration to the cathode were brought back to the anode zone where they could be reintroduced into the soil. After a few days of operation, the anode pH decreased from near neutrality to about 6 while the cathode pH effluent increased to over 12. The near neutral pH at the anode is thought to be partially due to the oxidation of the iron anode taking place preferentially over the electrolysis of water according to the following reactions:



This is consistent with the presence of rust in the anode solution. The pH of the anode solution was also neutralized by the high pH of the recycled cathode effluent. The pH in the center treatment zones did not vary much after the initial decrease from the starting pH of about 8 to a pH between 6 and 7 (Figure 8). The specific conductance of water in the treatment zones showed some fluctuations between 300 to 500 $\mu\text{S}/\text{cm}$.

Effects of Voltage Gradient. The relationship between the applied voltage gradient and the corresponding electro-osmotic flowrate was studied from about 1 V/cm down to below 0.1 V/cm. The electro-osmotic flowrate was found to vary quite linearly with the applied voltage gradient (Figure 9). Extrapolation of the fitted line shows that the flow would stop at a voltage gradient of 0.06 V/cm, or an overall voltage of about 7 volts. This threshold voltage is the sum of the voltages required to drive the electrode reactions and the overvoltages associated with our particular experimental setup. The results suggest that for a much larger setup (field-scale) where the overall voltage applied will be much higher than 7 volts, electro-osmosis can be operated efficiently at very low voltage gradients. For example, a 0.1 V/cm gradient for a 10 m electrode spacing would result in a total voltage of 100 V. The low voltage gradient is attractive in field operations due to less energy consumption per unit of

water transported electro-osmotically. Another benefit of low voltage gradient operations is less severe soil heating, as addressed below.

Soil Heating. Soil heating will occur in the use of electrokinetics for soil remediation due to the electrical input. While heating has not been an issue in laboratory studies, our modeling work discussed in the next section suggests that in field scale applications thermal effects of Joule heating will be significant. Under steady-state conditions, the energy supplied to the soil by Joule heating is balanced by thermal conduction of the energy to the boundaries of the soil system. As the size of the treated soil increases, the surface area to volume ratio decreases, and the characteristic length for heat conduction increases. This leads to a maximum steady-state temperature rise in the soil that varies with the square of the characteristic length of the region. Therefore, field experiments, which may easily be a factor of ten larger than laboratory experiments, might be expected to have temperature rises on the order of 100-fold larger than the similar laboratory experiment. Temperature rises as a function of the voltage gradient applied were measured to assess the importance of this effect and to provide data for the modeling effort.

Figure 10 shows the core soil temperature of the pilot unit (at the center of the soil mass) as a function of the applied voltage gradient. At 0.5 V/cm, the core temperature only went up to almost 25°C, an average of 1.1 degree above the ambient temperature of 23.7°C. When the voltage gradient was increased to 1.0 V/cm, the core temperature increased over several days to an average of 4.8°C over ambient. The voltage gradient was then doubled again to 2.0 V/cm. This caused a dramatic increase in soil core temperature, which within one week was approaching 53°C, a temperature rise of almost 30°C! The temperature rise appears to be roughly proportional to the square of the voltage gradient, consistent with the power input varying with the square of the applied voltage.

An increase in soil temperature could have an impact on volatile matter in the soil as well as electrokinetic effects. If the contaminant of interest is volatile, provisions should be made to monitor the air space above the treated area and control options evaluated.

Modeling of Thermal Effects

The significant temperature rises observed in the pilot experiments prompted the development of the following mathematical model describing Joule heating and heat transfer by conduction and convection (13).

The coupled equations describing the electric and temperature fields are:

Charge conservation:

$$\nabla \cdot \mathbf{s}(T) \nabla \mathbf{f} = 0 \quad (4)$$

Electro-osmotic and hydraulic flow through porous media:

$$u = -\frac{k_e(T)}{n} \Delta f - \frac{k_h}{nm} \Delta p \quad (5)$$

Energy conservation:

$$\frac{\partial T}{\partial t} = \frac{k}{r c} \nabla^2 T - nm \frac{r_w c_w}{r c} \bullet \nabla T + \frac{s(T)}{r c} - \nabla f \quad (6)$$

where f is the electric potential, s the electrical conductivity, u the pore fluid velocity, k_e the soil electro-osmotic permeability, k_h the soil hydraulic permeability, m the pore water viscosity, n the soil porosity, T the soil temperature, r the soil density, c the specific heat of the soil, r_w the pore water density, c_w the pore water specific heat, and k the thermal conductivity.

Equation 4 makes several simplifying assumptions regarding charge transport in the soil. First, there are no capacitive effects, which should be the case with a DC electric field. Second, charge is transferred predominantly by ionic migration, so that convection in the charged double layer at the soil particle/pore liquid interface and current carried by diffusion of ions are negligible. And third, the electrical conductivity, to first order, is only a function of temperature. Several investigators (2,14-18) have examined the transport of ions in electrokinetic applications, both experimentally and theoretically, and have shown that electrical conductivity becomes a strong function of position as ions get redistributed by the electric field and electrode reactions. However in soils with moderate buffering capacity it can be shown that this effect can be neglected in certain cases, including the laboratory tests simulated in this work.

Because both fluid viscosity and electrical conductivity are very sensitive to temperature, their temperature dependence has been incorporated in this model. The viscosity dependence is reflected by the electro-osmotic permeability, k_e , which varies inversely with viscosity, according to the Helmholtz-Smoluchowski equation (19). That is, the effects of temperature on the zeta potential, dielectric constant, and solubility of species are ignored. The following expression for the temperature dependence of viscosity of water (20) was used to estimate the temperature dependence of the electro-osmotic permeability:

$$\log_{10} \left(\frac{k_e(T)}{k_e(20^\circ C)} \right) = -\log_{10} \left(\frac{\eta(T)}{\eta(20^\circ C)} \right) = \frac{1.3273(T - 20^\circ C) + 0.001053(T - 20^\circ C)^2}{(T - 20^\circ C) + 125} \quad (7)$$

Laboratory experiments determined that the temperature dependence of soil electrical conductivity can also be expressed as a function of fluid viscosity (13). The inverse relation between electrical conductivity and fluid viscosity is consistent with the behavior of ionic aqueous solutions (21). Thus the temperature dependence of conductivity was also expressed in terms of fluid viscosity as

$$s(T) = s(20^\circ C) \frac{\eta(20^\circ C)}{\eta(T)} \quad (8)$$

A two dimensional rectangular geometry (1.1 m x 0.45 m) was used to represent the experimental apparatus used in these experiments. The left side of the rectangle was the anode and the right side was the cathode. The boundary conditions for the electric field were $f(\text{anode}) = f_0$ (60, 120 or 240 V) and $f(\text{cathode}) = 0$. The top and bottom sides of the rectangle was electrically insulated. The thermal boundary conditions are constant temperature of 23.7°C at all four sides of the domain. The parameters used in the example computer simulation are given in Table 4.

The thermal model was run for three applied voltages, 60, 120, and 240 V. Three cases are analyzed for maximum soil temperature, power and flow rate. The calculated maximum temperatures for these cases are shown in Figure 11. For this geometry, the warmest region lies in the center of the domain, and from the symmetry of the temperature field, it can be concluded that electro-osmotic convection is unimportant in heat transfer. This may not be the case if arrays of cylindrical electrodes are used. In such cases, maximum temperature may occur near the electrodes where the current is concentrated.

From Figure 11 it can be observed that the temperature rises begin relatively rapidly and then converge toward a steady value after about 7 days. The time scale for thermal diffusion across the narrow dimension of the geometry ($L^2 \rho c / k$) is 7.2 days. In field applications in which the characteristic dimension is, for example, 10 m, the steady state temperatures would not be reached until 3500 days, or well after the remediation was completed. The steady state temperature rises were 1.4, 6.6, and 30.3°C for the 60, 120, and 240 V cases respectively. This compares well with experimental measurements of 1.3, 4.9, and ~30°C for the respective conditions. The fact that the measured temperature rises are slightly smaller than the model predictions may be attributable to inaccuracies in input properties (the thermal conductivity was chosen to achieve a good fit with experimental data; other properties were measure independently), and the fact that a two-dimensional model was used to represent a three-dimensional experiment, and therefore the model had less effective heat transfer area. The factor of 4.7 between the temperature rise for the 120 V case and the 60 V case is slightly higher than the order of magnitude scaling which predicts that the temperature rise will be proportional to the electric field squared. The nonlinearity of the system, however, is more apparent when comparing the 60 V and 240 V cases. The ratio of temperature rises predicted in the simulations was 21.6 (the ratio of the corresponding temperature rises in the experiments was 23.1) compared to the factor of 16 that would be expected in a linear system.

The increased temperature rise at higher voltages is attributable to the temperature dependency of the electrical conductivity. As the conductivity increases, the V^2/R losses increase, because the system resistance goes down. Therefore the power supplied to the soil increases with time as shown in Figure 12. The transient behavior of the applied power is clearly dependent on the control strategy. If, instead of constant voltage, a constant current were maintained, the power (I^2R) would decrease with time as a result of decreasing resistance. In fact, operating at constant current in field scale applications has the important advantage of heating the soil relatively quickly early in the process, and approaching the steady state operating conditions faster than a constant voltage control system.

The effect of heating on the electro-osmotic flow rate is shown in Figure 13. The pore volumes as defined in Figure 13 refer to one-half of the total pore volume between the electrodes, because in the test there was one activated carbon treatment zone between the electrodes. As with the temperature rise, nonlinearity is seen in the relation between applied voltage and electro-osmotic flow. The ratio of the flow rate in the 240 V case to the 60 V case is 5.5, or 38% larger than if the electro-osmotic permeability were independent of temperature.

SUMMARY AND CONCLUSIONS

A novel integrated *in situ* remediation technology, called LasagnaTM, is being developed coupling electro-osmosis with in situ treatment zones. Experiments were conducted with kaolinite and an actual soil in units ranging from bench-scale containing kg-quantity of soil to a pilot-scale containing about half a ton of soil having various treatment zone configurations. The obtained data support the feasibility of scaling up this technology with respect to electrokinetic parameters as well as removal of organic contaminants. A mathematical model was developed that was successful in predicting the temperature rises in the soil. The information and experience gained from these experiments along with the modeling effort had enabled us to successfully design and operate a larger field experiment at a DOE TCE-contaminated clay site.

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REFERENCES

1. L. J. Casagrande, *BSCE*, 39:51-83 (1952).

2. A.P. Shapiro, P. Renaud, and R. Probstein, "Preliminary Studies on the Removal of Chemical Species from Saturated Porous Media by Electro-osmosis" In *Physicochemical Hydrodynamics*, Vol. 11, No. 5/6, pp. 785-802 (1989).
3. J. Hamed, Y.B. Acar and R.J.Gale, *ASCE*, Vol. 112, pp. 241-271, February (1991).
4. C. J. Bruell, and B. A.Segall, *J. Environ. Eng.*, Vol. 118, No. 1, pp. 68-83, Jan/Feb 1992.
5. B. A.Segall, and C. J. Bruell, *J. Environ. Eng.*, Vol. 118, No. 1, pp. 84-100, Jan/Feb 1992.
6. Y.B. Acar, H. Li, and R.J. Gale, *ASCE*, Vol. 118, No. 11, pp. 1837-1852, November 1992.
7. A.P. Shapiro, and R.F. Probstein, *Environ. Sci. Technol.* 27, pp. 283-291, 1993.
8. R. Lageman, "Electroreclamation - Applications in The Netherlands" *Environ. Sci. Technol.*, pp 26480, Vol. 27, No. 13, 1993.
9. Y. B. Acar and A. N. Alshawabkeh, "Principle of Electrokinetic Remediation" *Environ. Sci.Technol.*, pp. 2638-47, Vol. 27, No. 13, 1993.
10. S. V. Ho, P. W. Sheridan, C. J. Athmer,, M. A. Heitkamp, J. M. Brackin, D. Weber, and P. H. Brodsky "Integrated *In Situ* Soil Remediation Technology - The Lasagna Process," *Environ. Sci. Technol.*, 1995, 29(10), 2528-2534.
11. P.H. Brodsky and S.V. Ho, U.S. Patent No. 5,398,756, March 1995. The term Lasagna is a trademark of Monsanto Company.
12. L. Murdoch, "Some Recent Development in Delivery and Recovery: Hydraulic Fracturing and Directional Drilling" *Proceedings of ETEX'92 - The 2nd Annual Environmental Technology Exposition and Conference*, Wash., DC, USA, April 7-9, 1992.
13. Shapiro, A.P.; Schultz, D.S. *Emerging Technologies in Hazardous Waste Management VII*, 1995 Extended Abstracts for the Special Symposium, Atlanta, GA., American Chemical Society, p 457.
14. Alshawabkeh, A.N.; Acar, Y.B., *J. Environ. Sci. Health*, 1992, A27(7), 1835.
15. Eykholt, G.R.; Daniel, D.E. *J. Geotechnical Eng.* 1994, 120(5), 797.
16. Jacobs, R.A.; et al. *J. Environ. Sci. Health*, 1994, A29(9), 1933.
17. Hicks, R.E.; Tondorf, S. *Environ. Sci. Technol.*, 1994, 28(12), 2203.
18. Jacobs, R.A.; et al. *AICHE*
19. Probstein, R.F., *Physicochemical Hydrodynamics, An Introduction*, 1994, 2nd edition, John Wiley & Sons, Inc., New York, p. 197.
20. Weast, R.C., ed. *Handbook of Chemistry and Physics*, 1972, The Chemical Rubber Co., Cleveland, p F-36.
21. Gurney, R.W. *Ionic Processes in Solution*, 1953, Dover Publications, New York, p 69.

Table 4. Model Parameters

Parameter	Value
porosity, n	0.4
thermal conductivity, k	$1.2 \text{ W m}^{-1} \text{ K}^{-1}$
electrical conductivity, s_0 (20°C)	0.024 S m^{-1}
Pore fluid viscosity, μ (20°C)	$0.001 \text{ kg m}^{-1} \text{ s}^{-1}$
soil density, ρ	1970 kg m^{-3}
soil heat capacity, c	$1870 \text{ J kg}^{-1} \text{ K}^{-1}$
water density, ρ_w	1000 kg m^{-3}
water heat capacity, c_w	$4180 \text{ J kg}^{-1} \text{ K}^{-1}$
electro-osmotic permeability, k_e (20°C)	$1.2 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$